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Cross-linked Poly-(4-vinylpyridine–styrene)–Bromine Complexes as Stereoselective Brominating Agents

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Cross-linked poly(styrene–4-vinylpyridine) beads, containing 40—43% of pyridine rings, were transformed with bromine to provide three types of brominating agents (1), (2), and (3). Reactions of *cis*- and *trans*-1-phenylpropene with (1), (2), and (3) resulted in a high degree of *anti*-stereoselectivity. The reactivity increases from (1) to (3); solvent polarity has no significant effect on stereoselectivity, but affects the reactivity, being significantly greater in acetonitrile and chloroform than in cyclohexane and dioxan. Bromination of 1-phenylcyclohexene with (1) and (3) resulted in the formation of *trans*-1,2-dibromo-1-phenylcyclohexane (9) and 3-bromo-2-phenylcyclohexene (10), the temperature affecting only the ratio of the products. Bromination of norbornene with the reagents (1), (2), and (3) resulted in the formation of seven products: 2-*exo*-bromonorbornane (12), 7-bromonortricyclane (13), 2-*exo*, 3-*endo*-dibromonorbornane (14), 2-*exo*-7-*anti*-dibromonorbornane (15), 2-*exo*, 5-*endo*-dibromonorbornane (16), 2-*exo*, 5-*exo*-dibromonorbornane (17), and 2-*exo*, 7-*syn*-dibromonorbornane (18).

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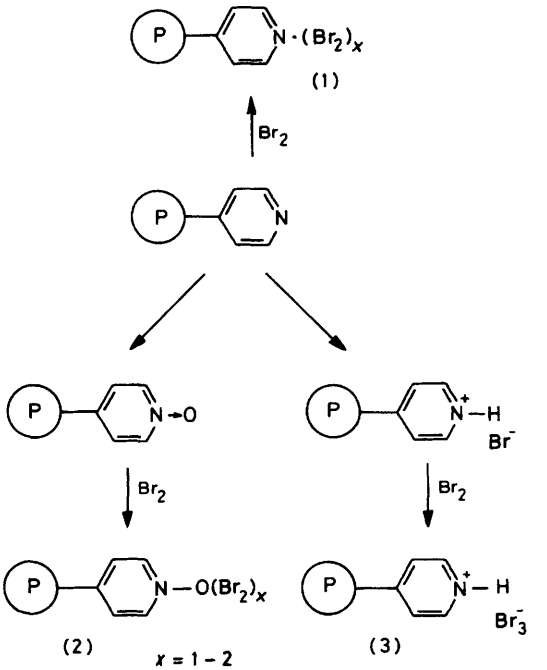
POLYMER beads have found a wide range of uses in organic chemistry, cross-linked polystyrene resins usually being used, while cross-linked poly(vinylpyridine) or cross-linked copolymers with styrene and vinylpyridine have received much less attention.[1] Pyridine has broad applications in organic synthesis by itself or in conjunction with other reagents. Poly(vinylpyridine) was found to be useful as an HCl acceptor,[2] poly(vinylpyridinium hydrobromide perbromide) resins were useful as brominating agents,[3] poly(vinylpyridinium chlorochromate) has been used as an oxidising agent,[4] poly(vinylpyridine borane) complex as a reducing agent,[5] polyvinylpyridine as a matrix for protein immobilisation,[6] and the poly(vinylpyridine)–copper as a complex catalyst for polymerization.[7]

The stereochemistry of bromine addition to alkenes depends on the substituents bonded to the double bond, solvent polarity, temperature, and the reagent used.[8] Recently, it has been demonstrated that *anti*-addition of bromine could be favoured by using the dibenzo-18-crown-6–bromine complex,[9] the stereoselectivity being markedly higher than in the case of the pyridine–bromine complex.

Recently we have synthesized various halogen (F, Cl, and Br) complexes with cross-linked poly-(4-vinylpyridine–styrene), and found that only the bromine complexes reacted with 1,1-diphenylethene, forming 1,2-dibromo-1,1-diphenylethane and 2-bromo-1,1-diphenylethane in chloroform, while reaction in methanol also produced 2-bromo-1-methoxy-1,1-diphenylethane.[10] We have extended our investigation to the stereochemistry of bromine addition to various alkenes with polymer-supported bromine complexes where the stereochemistry of addition with other reagents is known, thus enabling us to obtain information on the effect of the polymer resins on the stereochemical course of the reaction.

RESULTS AND DISCUSSION

In the present study we synthesized a copolymer of styrene and 4-vinylpyridine in the presence of 2% of divinylbenzene, the beads thus obtained containing 40—43% of pyridine rings. Reaction in chloroform in the presence of excess of bromine resulted in the formation of a complex containing 50.1 % of bromine, which means that >60% of the pyridine rings are associated with four bromine atoms (1; Scheme 1). A high proportion of bromine bonded to the polymer resin was also found by mixing cross-linked poly(styrene–4-vinylpyridine *N*-oxide) resins [prepared by oxidation of poly(styrene–4-vinylpyridine)] with bromine (2; 47.4% of bromine). The third reagent (3) was prepared by reaction of cross-linked poly(styrene–4-vinylpyridine) with hydrogen bromide and bromine, and contained 41.5% bromine, which corresponds to a degree of functionalization of >85%.



SCHEME 1

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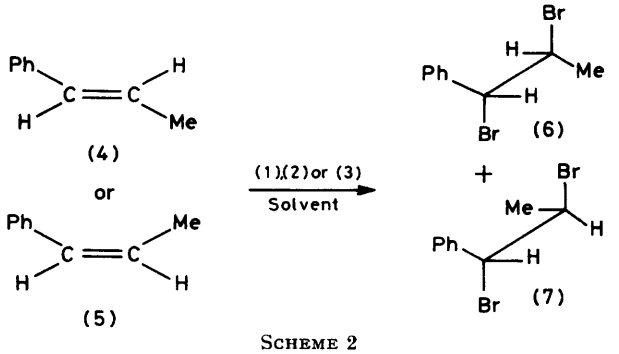
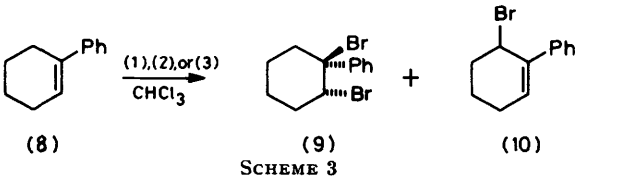
First we studied the stereochemistry of bromine addition to *trans*-(4) and *cis*-1-phenylpropene (5) with the reagents (1), (2), and (3) at room temperature (Scheme 2). Each experiment was repeated several times and the



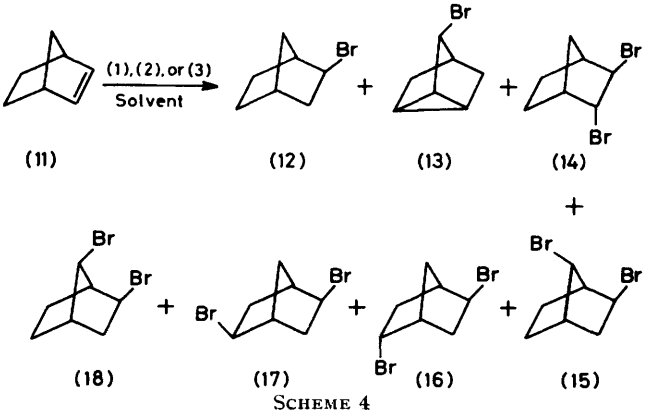
Scheme 2

crude reaction mixtures were analysed by ^1H n.m.r. spectroscopy. The reactions with both olefins are highly stereoselective and solvent polarity has no significant effect on the stereochemistry of bromine addition. The reactivity of the polymer-supported brominating reagents increases from (1) to (3), while the reactivity is lowered markedly in cyclohexane and 1,4-dioxan, compared to that in chloroform and acetonitrile. A comparison of the present results for the *anti*-addition of bromine to *cis*- and *trans*-1-phenylpropene using (1), (2) and (3) with literature results for the reactions with bromine, the pyridine–bromine complex, and the dibenzo-18-crown-6–bromine complex is in Table 1.



Scheme 3

by bromide in methylene dichloride for comparison. The effects of the reaction temperature and of the concentration of norbornene in its reaction with (2) in acetonitrile and methylene dichloride are presented in Table 4. As regards the stability of the products under the reaction conditions, we did not observe any appreciable change in the distribution of the products (12)—(18) with shorter or longer reaction times. The presence of



Scheme 4

Table 1

% of anti-Addition of bromine to *cis*-(5) or *trans*-1-phenylpropene (4)

Solvent	(1)	(*t*/h)	(2)	(*t*/h)	(3)	(*t*/h)	Br_2[9]	Pyridine–Br_2[9]	Dibenzo-18-crown-6-Br_2[9]
trans-1-Phenylpropene (4)									
C_6H_{12}	100	(20)	100	(24)	98	(5)	92	—	100
$CHCl_3$	100	(3.5)	100	(3)	100	(3.5)	—	—	—
MeCN	100	(3.5)	98	(2.5)	100	(1.5)	89	90	100
$C_4H_8O_2$	98	(20)	98	(5)	98	(1.5)	79	89	100
cis-1-Phenylpropene (5)									
C_6H_{12}	98	(26)	100	(24)	98	(5.5)	85	—	100
$CHCl_3$	98	(4)	100	(4.5)	100	(4)	—	—	—
MeCN	98	(3)	100	(1.5)	98	(3.5)	69	59	98
$C_4H_8O_2$	95	(26)	93	(24)	94	(1.5)	25	46	25

The bromination of 1-phenylcyclohexene (8) depends on the conditions, and up to five products are formed.[11] Reactions with reagents (1) or (3) at room temperature or at 62 °C in chloroform resulted in the formation of only two products [(9) and (10); Scheme 3]. An increase in temperature led to an increase in the amount of 3-bromo-2-phenylcyclohexene (Table 2).

The bromination of norbornene (11) with bromine has been studied in detail and seven products were formed.[12] The reactions with the polymer-supported reagents (1), (2), or (3) also gave seven products [(12)—(18); Scheme 4]. The effects of the structure of the polymer-supported reagent and of solvent polarity on the product composition are shown in Table 3, with the results for bromination oxygen as an inhibitor of carbon-centred radicals also had no influence on the product distribution. The effects of solvent on the composition of the dibromide fraction from addition of bromine to norbornene with the reagent (2) and with bromine are in Table 5. The most significant difference in the ionic pathways of the

Table 2

Product distribution (%) in the bromination of 1-phenylcyclohexene (8) in chloroform

Reagent	Time (h)	Temp. (°C)	(9) : (10)
(1)	4	25	77 : 23
	3	62	50 : 50
(3)	3	25	82 : 18
	3	62	44 : 56

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TABLE 3

Product distribution in the bromination of norbornene (11) [a]

Reagent	Solvent	Products (%) (12)	(13)	(14)	(15)	(16)	(17)	(18)
(1)	MeCN	20.2	15.4	15.9	31.3	8.8	8.4	—
(2)	MeCN	24.8	10.0	14.2	32.5	9.4	9.1	—
(3)	MeCN	30.2	10.3	13.1	29.8	8.5	8.1	—
(2)	CH_2Cl_2	21.5	17.9	7.1	10.5	2.9	2.4	37.7
Br_2 [b]	CH_2Cl_2	16.7	34.4	3.0	12.4	3.1	1.9	27.3
(1)	$CHCl_3$	13.2	19.0	14.0	7.7	1.7	1.5	42.9
(2)	$CHCl_3$	12.5	21.1	12.0	10.8	2.6	2.6	38.6
(3)	$CHCl_3$	17.1	15.8	9.7	9.0	1.8	1.5	45.1
(2)	CCl_4	0.9	26.7	12.7	10.5	2.3	1.9	45.0

[a] Each experiment was repeated several times, average data being presented, and relative yields were determined by g.l.c. maximum error is ±1.5%; concentration of norbornene 10 mg/ml, reaction time 210 min at 23 °C. [b] Ref. 12, concentration of norbornene 4.98 mg/ml, $T = 0$ °C.

TABLE 4

Variation of product distribution with solvent, concentration, and temperature in the bromination of norbornene (11)

Solvent	[Norbornene]/ mg/ml	Temp./°C	Products (%) (12)	(13)	(14)	(15)	(16)	(17)	(18)
MeCN	10	0	9.8	11.6	15.9	36.3	13.5	12.9	—
MeCN	1.5	23	0.4	31.1	13.3	30.8	12.8	9.6	2
MeCN	30	23	27.8	13.3	10.2	24.5	5.4	5.9	12.9
MeCN	10	50	35.6	12.4	11.4	25.6	7.7	7.3	—
CH_2Cl_2	2.5	23	5.5	25.6	5.8	13	3.7	3	43.4
CH_2Cl_2	20	23	13.9	16.4	11.8	8.4	2.1	1.8	45.6

TABLE 5

Effect of solvent on the composition of the dibromide fraction from the addition of bromine to norbornene (11) with (2) [a] and Br_2 [b]

Solvent	Reagent	Normalized % of dibromides (14)	(15)	(16)	(17)	(18)
CCl_4	(2)	17.5	14.5	3.2	2.6	62.2
CCl_4	Br_2	7—9	15—17	1.6—2.3	1.6—2	66—71
CH_2Cl_2	(2)	11.7	17.3	4.8	4	62.2
CH_2Cl_2	Br_2	6.2—7	21—22	6.7—7.1	3—3.6	56—59
MeCN	(2)	21.8	49.9	14.3	14	—
MeCN	Br_2	2.3—3	13—17	0.6	2	77—82

[a] Concentration of norbornene 10 mg/ml, reaction time 210 min, at 23 °C. [b] Ref. 12, concentration of norbornene 10 mg/ml, $T = 0$ °C.

two brominations is found in acetonitrile, where in the case of reagent (2) 2-*exo*-7-*syn*-dibromonorbornane (18), the main product in bromination with bromine, was not observed. However, similar decreases in the amount of (18) formed were also observed in bromination with bromine in methylene dichloride when the solution was saturated with tetraethylammonium bromide.[12]

The polymer-supported brominating reagents (1), (2), and (3) could be recovered easily after reaction and re-used several times without loss of activity.

EXPERIMENTAL

I.r. spectra were recorded using a Perkin-Elmer 727 B instrument, and ^{1}H n.m.r. spectra on a Jeol JNM-PS-100 spectrometer with Me_4Si as internal reference. Mass spectra were taken on a CEC-21-110 spectrometer. Gas–liquid partition chromatography was carried out on a Varian Aerograph, Model 3 700, and CDS 111 integrator.

Materials.—The polymer-supported brominating agents (1), (2), and (3), were prepared as described,[10] and *cis*- and *trans*-1-phenylpropene [14,15] and 1-phenylcyclohexene [16] were synthesized. Solvents were purified and stored over molecular sieves.[13]

Addition and Isolation Procedures.—To a stirred solution of the alkene (0.5 mmol) in the appropriate solvent (10 ml) was added the polymeric reagent (1), (2), or (3) (500 mg) at 23, 25, or 62 °C. The mixture was stirred for 1—26 h and diluted with solvent (5 ml), the polymer was filtered off and washed twice with solvent (5 ml), and the solution and washings were evaporated *in vacuo*. The products isolated in high yields, were analysed by ^{1}H n.m.r. spectroscopy for the reactions of *cis*- (5) and *trans*-1-phenylpropene (4) and 1-phenylcyclohexene (8), and by g.l.c. for norbornene (11). Each experiment was repeated several times and the maximum error in the determination of the composition is ±1.5 %. The structures of the products were determined by spectroscopic comparison with authentic samples prepared independently by literature methods.[9,11,12]

Determination of the Active Bromine Content of the Polymeric Reagents (1), (2), *and* (3) *and Regeneration of the Polymer Resins*.—The reactions of the brominating reagents (1), (2), and (3) with aqueous potassium iodide resulted in the formation of iodine which, however, is readily bonded to the polymer resins, thus preventing the determination of the

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amount of active bromine by titration with sodium thiosulphate. Hence in order to determine the active bromine reactions were carried out with an excess of olefin, and the mixtures analysed by ^1H n.m.r. spectroscopy. To a solution of 1,1-diphenylethene (1 mmol) in methanol (10 ml) the polymer reagent (1), (2), or (3) (0.25 g) was added and the mixture heated under reflux for 4.5 h. The resulting mixture, containing 1,1-diphenylethene, 2-bromo-1,1-diphenylethene, 1,2-dibromo-1,1-diphenylethane, and 2-bromo-1-methoxy-1,1-diphenylethane was analysed by ^1H n.m.r. spectroscopy and the following activities were observed (in mmol of Br_2/g of reagent): 2.3 for (1), 2.5 for (2), and 1.7 for (3). For the regeneration of reagent (3) from the polymer resins isolated after the reaction of (3) with the olefins, only washing with methanol and chloroform was needed, prior to the reaction with bromine, whereas the reagents (1) and (2) required stirring of the resins with a 2M-aqueous sodium hydroxide at 40—50 °C for 5 h. The use of higher concentrations of sodium hydroxide or higher temperatures resulted in decomposition of the polymer resins. The i.r. spectra of the polymer resins isolated after work-up with sodium hydroxide showed no significant difference from those of the polymer resins used initially in the reactions leading to (1), (2), or (3); the resins could be re-used at least ten times for the preparation of the brominating reagents.

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